

# PATENT SPECIFICATION

(11) 1 230 854

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## DRAWINGS ATTACHED

- (21) Application No. 22920/68 (22) Filed 14 May 1968
- (31) Convention Application Nos. 638 428 and 638 647
- (32) Filed 15 May 1967 in
- (33) United States of America (US)
- (45) Complete Specification published 5 May 1971
- (51) International Classification B 01 j 13/02; C 08 g 45/04; F 16 b 39/22
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 1L6A 1L6D 1N11 1N18X 1N1A 1N1F 1N1G  
 1N1N 1N2B 1N6A 1N6D1 1N6D2 1N6D3  
 1N6D4 1N6D5 1N6D6 1N6D8



## ERRATUM

SPECIFICATION NO. 1, 230, 854

Page 1, line 1, for '&' read 'AND'

THE PATENT OFFICE  
1 October 1971

R 5:

10 a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

15 This invention relates to improved self-locking mechanical fasteners, particularly those employing threaded parts, such as bolts, screws, nuts, pipe joints and threaded nails, and to the stable latent curing adhesive cements suitable for use in conjunction therewith. The invention also relates to a process of preparing the cements.

20 One fastener sealing adhesive system in present commercial use involves an anaerobically curable adhesive which is applied to the fastener in liquid form immediately before the fastener is to be installed. Such systems suffer from the disadvantage that they must be applied by the ultimate user of the fasteners, rather than by the fastener manufacturer, and once cure is completed, refastening cannot occur.

30 Another system is that in which two separated strips of co-reactants are applied to the threads of a bolt. This system requires two separate applications of the adhesive materials, and generally a further application of a protective polymer coating. The bolts cannot easily be shipped in contact with other because of the likelihood of contact and premature reaction of the coreactants due to contact of resin on one bolt with curing agent on another.

40 Another system which has been proposed is that in which a latent curing single-component adhesive is coated on the abutment surfaces

11 but not hitherto fully understood. Apparently the commercially used capsules, formed from aminoplast polymers, are not entirely impervious especially after long term storage in contact with many amine epoxy curatives. These amines, especially in the presence of moisture, appear to swell or other wise attack the capsule walls, causing premature cure of the adhesive with resultant loss of adhesive locking strength. Amines such as aminoethyl piperazine, which are capable of curing epoxy resins at room temperature apparently volatilize and escape from the adhesive over too short a storage period. Other less volatile amines, such as dicyandiamide either will not cure the resin at room temperature or are immiscible with the resin when released from the capsules; thus the adhesive does not cure rapidly, if at all, at room temperature. The more volatile amines apparently vapourise and escape, even when covered by a coating of a material such as methyl cellulose.

The water-based, hygroscopic methyl cellulose binder apparently in itself causes instability due to its tendency to pick up moisture from the surroundings. Instability due to water is unexpected since the capsules are manufactured in an aqueous slurry and are found stable in the presence of moisture in other applications. Unknown forces, perhaps the water in combination with an amine curative, apparently cause the instability which can be overcome in accordance with the present invention.

According to the present invention there is

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(11) 1230854

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 1N6D4 1N6D5 1N6D6 1N6D8

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## (54) FASTENERS, SEALANTS THEREFOR, AND PROCESS

(71) We, MINNESOTA MINING & MANUFACTURING COMPANY, a Corporation organised and existing under the laws of the State of Delaware, United States of America of 2501 Hudson Road, Saint Paul, Minnesota 55101, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to improved self-locking mechanical fasteners, particularly those employing threaded parts, such as bolts, screws, nuts, pipe joints and threaded nails, and to the stable latent curing adhesive cements suitable for use in conjunction therewith. The invention also relates to a process of preparing the cements.

One fastener sealing adhesive system in present commercial use involves an anaerobically curable adhesive which is applied to the fastener in liquid form immediately before the fastener is to be installed. Such systems suffer from the disadvantage that they must be applied by the ultimate user of the fasteners, rather than by the fastener manufacturer, and once cure is completed, refastening cannot occur.

Another system is that in which two separated strips of co-reactants are applied to the threads of a bolt. This system requires two separate applications of the adhesive materials, and generally a further application of a protective polymer coating. The bolts cannot easily be shipped in contact with other because of the likelihood of contact and premature reaction of the coreactants due to contact of resin on one bolt with curing agent on another.

Another system which has been proposed is that in which a latent curing single-component adhesive is coated on the abutment surfaces

of threaded fastening devices. Co-reactants which together form the adhesive are separated from each other by encapsulation in microscopically small capsules which rupture upon the application of pressure to mix the co-reactants thus activating the adhesive. However, such systems suffer from a lack of stability not hitherto fully understood. Apparently the commercially used capsules, formed from aminoplast polymers, are not entirely impervious especially after long term storage in contact with many amine epoxy curatives. These amines, especially in the presence of moisture, appear to swell or other wise attack the capsule walls, causing premature cure of the adhesive with resultant loss of adhesive locking strength. Amines such as aminoethyl piperazine, which are capable of curing epoxy resins at room temperature apparently volatilize and escape from the adhesive over too short a storage period. Other less volatile amines, such as dicyandiamide either will not cure the resin at room temperature or are immiscible with the resin when released from the capsules; thus the adhesive does not cure rapidly, if at all, at room temperature. The more volatile amines apparently vapourise and escape, even when covered by a coating of a material such as methyl cellulose.

The water-based, hygroscopic methyl cellulose binder apparently in itself causes instability due to its tendency to pick up moisture from the surroundings. Instability due to water is unexpected since the capsules are manufactured in an aqueous slurry and are found stable in the presence of moisture in other applications. Unknown forces, perhaps the water in combination with an amine curative, apparently cause the instability which can be overcome in accordance with the present invention.

According to the present invention there is

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provided a mechanical fastener having on abutment surfaces thereof a coating of a locking cement which is pressure-activatable and self-curing at ambient temperatures to give a  
 5 firmly adherent bond and which comprises microscopically small capsules containing therewithin a liquid resin, the capsules being rupturable upon application of pressure, a  
 10 substantially non-volatile curing agent for the resin which is miscible therewith and a non-hygroscopic substantially non-tacky and water-free organic polymeric binder in which the microcapsules and curing agent are homogeneously dispersed.

Also according to the present invention there is provided a stable latent room temperature curable adhesive cement composition which can be applied on surfaces to be bonded to form a  
 20 stable solid substantially non-tacky coating which is pressure-activatable and self-curing at ambient temperatures to give a firmly adherent bond, comprising microscopically small capsules containing therewithin a liquid polyepoxide resin, the capsules being rupturable  
 25 upon application of pressure, a substantially non-volatile curing agent for the polyepoxide resin which miscible therewith and a non-hygroscopic substantially non-tacky and water-free organic polymeric binder in which the  
 30 microcapsules and curing agent are homogeneously dispersed.

The fasteners according to the invention are a significant advance over the prior art in that they are self-locking, permit the use of known  
 35 capsules for containing an adhesive co-reactant, and have the commercially required stability and capability of withstanding prolonged storage and handling.

The mechanical fasteners according to the invention are easily used by the fastener manufacturer. The preferred adhesives are tack-free and non-blocking so that many fasteners can be shipped and stored without adhering to each other or being tacky to the touch. The  
 45 preferred adhesives, when applied to the fastener, have long term stability both before and after application so that both the adhesive and the coated fasteners may be handled and stored in accordance with conventional  
 50 procedures without degrading the adhesive. In use, the fastening device is readily applied without undue increase in the input torque necessary to install the fastener. The bonds formed resist vibration encountered in industrial machinery, refrigerators and automobiles.  
 55 The preferred adhesives of this invention cure rapidly so that the fastener may be used after only a short cure period and substantially increase back-off torque required to remove the fastener. The adhesives are capable of reuse after removal of the fastener, and provide  
 60 some latent curing which would enable a loosened fastener to become refastened rather than dropping out of place. Fastener systems which  
 65 have been previously available have not had all

of these features and suffer from one or more drawbacks.

The adhesive cement composition of this invention, prior to application to a mechanical fastener, can be shipped in commerce and  
 70 stored for weeks or months without premature cure and can then be applied to fasteners and then further stored for extended periods at ambient temperatures (which normally fluctuate widely), and cured at room temperature  
 75 upon physical rupture of the microcapsules. If desired, cure can be accelerated by the application of heat to the composition, but room temperature cures are ordinarily preferred for convenience of application. The cement composition of this invention can be applied in one  
 80 single coating process and can be applied to any surface of the fastener to which sufficient pressure is applied in use to cause rupture of the capsules. The threads of a threaded mechanical fastener are preferred because both  
 85 compressive and shearing forces are applied to the adhesive to rupture capsules and mix the co-reactants.

In accordance with the present invention, it has been discovered that certain preferred combinations of curing agents and binders can be used together with aminoplast polymer capsules to provide stable ostensibly one-part  
 90 adhesives which are not only non-tacky, but which are also stable in humid atmospheres. Preferred room temperature curing agents are readily miscible with the resin. Further applications of the adhesive may include flat surfaces which are joined together under great  
 95 pressure, preferably with simultaneous application of frictional shearing forces.

The improved cement compositions of this invention are substantially free of water and other polar solvents and contain non-hygroscopic ingredients including an encapsulated  
 105 resin, a substantially non-volatile resin-miscible curing agent, and an organic polymeric binder for the resin and curing agent. Since the adhesive systems are substantially water-free, corrosion of the fasteners is reduced to a minimum.

The improved self-locking fasteners of this invention are formed by applying the improved adhesives to the abutment surfaces thereof  
 115 especially to the threaded portion of a threaded mechanical fastener such as the threads of a nut or bolt. Such fasteners are generally formed from a rigid structural material such as metal, wood, glass, ceramic, or a plastics material such as nylon or polyvinyl chloride, and may include bolts, screws, nuts and pipe fittings. Other mechanical fasteners to which the improved adhesives may be applied include  
 120 dowels, nails, rivets and staples, in which case the adhesive is applied, for example, to the shank and/or under the head, of the fastener. The adhesive formulations can be applied to the fasteners by dipping, spraying, strip application of molten material extruded on the  
 125  
 130



fastener, roll application, or other techniques which will be apparent to those skilled in the art.

5 The invention will be further illustrated by the accompanying drawing which is an enlarged cross-sectional view of a fastener illustrating one embodiment of the invention.

10 Bolt 10 is coated, preferably on threads 12, with adhesive 14. The adhesive 14 preferably consists of a matrix portion which is a polymeric binder 18 having distributed therein capsules 20 (shown greatly enlarged) which contain a curable resin. A curing agent for the resin is also distributed throughout the binder matrix. As the nut 22, or equivalent mating threaded device, is run onto the bolt 10, some of the capsules 20 are ruptured by the shearing forces produced. The shearing forces caused by running the nut 22 onto the bolt 10 also effect thorough mixing of the resin released from the capsules with the curing agent, thus promoting rapid thorough cure of the released resin. Capsules not ruptured by the first use of the fastener can be ruptured on re-use of the fastener or upon movement of the fastener, for example, due to vibration. Thus, the fasteners of this invention are both reusable, and capable of refastening themselves if slightly loosened in use.

30 The preferred resins are liquid 1,2 - epoxy resins, containing within microscopically small capsules which range in size from 5 to 500 microns, and preferably 25 to 150 microns. Examples of the preferred epoxy resins include 1,2 - epoxy reaction products of polyhydric phenols such as bisphenol - A and epichlorohydrin or polyglycidyl ether, epichlorohydrin with phenol - formaldehyde condensation polymers and epichlorohydrin with amino phenols.

40 The preferred polyepoxides contain an average of more than 1 and generally an average of more than 1.5 oxirane groups per molecule. Examples of the preferred resins are liquid polyglycidyl ethers of bisphenol-A which have slightly less than two oxirane groups per average molecular weight (for example, Epon 815, or ERL-2795). Examples of resins having more than two oxirane groups per average molecular weight are polyglycidyl ethers of phenol-formaldehyde novolaks (for example, D.E.N. 438, which has a functionality of 3.6, or the trifunctional novolak Epiphen E.R. 823). When highly viscous resins such as the latter, or even solid resins are used, for example, in order to provide some desired property such as temperature resistance, it is preferred to form a blend with a less viscous resin such as ERL-2795. Further suitable resins include polyglycidyl ethers obtained from the reaction of dihydric or polyhydric alcohols with epichlorohydrin, for example, resins made by condensing epichlorohydrin and glycerin to give di- and tri-epoxides having a functionality of about 2.2 (e.g., Epon 182) and polyglycol polyepoxides such as the diglycidyl ether

of polypropylene oxide (e.g., D.E.R. 736). Further examples will be apparent to those skilled in the art.

70 For the preferred epoxy resin systems, it has been found that there are several important characteristics for the curing agent used. Firstly, the curing agent should cure the resin to a tough infusible state within 24 hours and preferably within 18 hours, at room temperature. Preferred curatives produce a significant amount of cure within a shorter time, within a few minutes up to about 6 hours. The curative should be capable of being stored at 120° F exposed to the atmosphere for at least one week without losing more than 2% of its weight. Curatives having this characteristic have been found to be useful in forming adhesives having long term storage stability on bolts or other fasteners at ambient temperatures. A third important characteristic is that an amine curing agent should desirably have at least 50 or more atomic weight units per amine group. Amines having a higher functionality than this (i.e., less than 50 molecular weight units per amine group), while often being good room temperature curatives, have been found to produce instability, apparently by attacking the walls of capsules formed from condensation polymers such as urea-formaldehyde. One preferred curing agent is an amine which will convert the polyepoxide resin at room temperature to a hard infusible state within eighteen hours after rupture of the capsules.

100 The preferred substantially non-volatile curing agent may be in either solid or liquid form so long as it is miscible with the resin used, i.e., will rapidly dissolve when mixed with the resin. Some useful amine curing agents will dissolve in the resin in significant amounts and cause an increase in viscosity within a day, but may require as much as 7 days to reach a hard resin stage. The latter curatives can be used in cases where longer cure times do not present a problem. For the purposes of this invention, it is critical that the curing agent be substantially non-volatile. Volatility can be determined by placing a weighed sample of the curing agent in an open vessel in a circulating air oven held at 120° F and observing the weight loss.

120 Examples of suitable substantially non-volatile amine curing agents for polyepoxide resins are imidazole, 1,3 - bis - 4 - piperidyl propane, 1,6 - hexane diamine, methylenedianiline, substituted alkylene diamines and liquid polyamide resins such as Versamid (Registered Trade Mark) 125 (a dimerized unsaturated fatty acid reacted with alkylene diamines). It will be understood that curing agents which are in themselves volatile can sometimes be converted by chemical reaction to a substantially non-volatile form. For example, liquid amines can be reacted with acids to form solid amine salts having reduced vapour

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pressure. For example, the tetraethylenepent-amine can be reacted with a fatty acid to give a salt useful as a curing agent.

5 The preferred amine curing agents for poly-epoxide resins are strongly basic amines which in saturated solution in water will have a pH value of at least 9.5. Amines more weakly basic than this tend to provide a cure rate for the adhesive less than the optimum. The  
10 curing agent is generally added in approximately a stoichiometric amount. However, those skilled in the art will recognize that lesser amounts can be used in the case of curatives which have a catalytic curing effect on the  
15 resin.

The binder resin used to bind together the capsules and curing agent should be substantially water-free, e.g. containing less than about 1% water, and should be an organophilic, hydrophobic organic polymeric material, preferably water insoluble, which will, on curing or drying of any solvent therefrom, result  
20 in a solid, non-tacky coating at room temperature on the fastener to which the adhesive composition is applied. This binder is added to the adhesive composition in amounts sufficient to bind the other ingredients in the adhesive together without crumbling or peeling away from the fastener surface. Generally  
25 somewhat larger amounts of binder resin are necessary in the case of liquid curing agents in order to provide a formulation which will dry to a solid substantially tack-free state. Examples of suitable binder materials include  
30 butadiene-styrene copolymers, either of the GRS or stereospecific block copolymer type, butadiene-acrylonitrile copolymers, polyvinyl butyral, butyl rubbers, solid polyamide resins and polyurethane resins.

40 In one preferred embodiment of the invention, the binder resin is dissolved in a solvent therefor and the capsules and curing agent are mixed therein. This mixture can then be applied to bolts or other fasteners, for example,  
45 dipping, brushing or spraying, and the mixture dries to a tack-free film upon evaporation of the solvent. Such solvents are preferably of a non-polar type, such as toluene or benzene.

In another embodiment of the invention, the  
50 binding resin is in the form of a relatively low temperature melting material. The adhesive composition is formed by melting the resin and mixing in the capsules and curing agent. The adhesive-containing mixture is then handled  
55 in a solid form, commonly referred to as a "hot melt". This "hot melt" formulation is applied to the fastener by melting and applying to the abutment surfaces of the fastener or may simply be applied by rubbing the formulation over a fastener, particularly the  
60 threaded portion thereof. The "hot melt" type formulations provide cost and safety advantages in that the use of the volatile solvent, which is usually lost on volatilisation, and

which may cause odour and fire hazards, is  
65 eliminated.

In a still further embodiment of the invention, the adhesive can be formed into a flexible film. Such films can be formed by using a polymeric binder which is a rubbery film-forming  
70 material containing the capsules and curing agent, and casting the same onto a flat surface in the form of either a molten or solvent-containing liquid, and hardening either by cooling or evaporating the solvent. Films thus formed  
75 can be stamped into washers which can then be applied to fasteners in the usual manner, or the film may be used as a thread wrapping means. In the latter applications, the film is simply wrapped around the threads before application of the mating threaded part, which causes rupture of the capsules due to the combined pressures in shearing forces. Such films can be wound and supplied in the form of a  
80 tape.

The capsules are generally spherically or spheroidally shaped discrete bodies, having diameters ranging from 1 to 2000 microns, and more preferably 25 to 150 microns for resin-containing capsules. These capsules are  
90 each composed of an outer continuous self-supporting shell wall of water-insoluble synthetic plastic, e.g. aminoplast polymer, surrounding an inner fill particle. In general, the fill material in each capsule comprises from 50 to 95 weight percent of the capsule with the shell making up the remaining 50 to 5 weight percent, although less fill may be used if desired. A discussion of aminoplasts and aminoplast precursors appears in C. P. Vale's book  
95 "Aminoplasts", Interscience Publishers, Inc. (1950).

Aminoplast polymers, and particularly urea-formaldehyde plastics, may be used in many different ways, in an effort to encapsulate oily  
105 fill materials, including resins, with no useful results or indifferent results. However, in our British Patent Specification No. 989,264 it is taught that if certain controls are exercised, it is possible to attain highly useful capsules. This result is especially impressive in the size range of 50 microns and less, e.g. 5 to 25 microns, more or less. These capsules are of sufficient toughness and impermeability to carry non-aqueous solutions of dye precursors, in contact with aqueous media containing color forming reactants for said dye precursors, without premature rupture or leakage. Further, these capsules can stand the rigors of paper formation of a paper machine and can be  
115 directly incorporated into a paper furnish in the formation of papers having the capsules carried as a filler therewithin.

Microencapsulation of water-insoluble fill material within a water-insoluble non-thermo-  
120 plastic synthetic resin of the aminoplast type is accomplished by providing (1) an aqueous solution of a water-soluble, low-molecular-

- weight urea-aldehyde precondensate comprising predominantly low molecular weight reaction products of urea and formaldehyde, e.g. dimethylol urea, the solution having a solids content of 3% to 30% by weight of the total aqueous precondensate, and into which is incorporated (2) water-insoluble fill material in an amount in parts by weight of about one-tenth of a part to about ten parts of fill material for each part solids in the precondensate, (3) dispersing the fill material as microscopically sized discrete particles in the solution in the substantial absence of wetting agents, and while continuing to maintain the fill material in particulate form and maintaining the resultant dispersion at a temperature of 10 to 50° C, (4) adding acid thereto in an amount to provide a pH for the dispersion in the range of 1 to 5.0 and more practically 1.5 to 3 or 3.5, thereby promoting acid catalysts of the precondensate, (5) continuing polymerization of the precondensate to a water-insoluble urea-formaldehyde polymer while maintaining the fill material as finely dispersed particles, viz, by rapid agitation within a temperature range 20 to 90° C for at least one hour, whereupon an aqueous slurry of capsules is provided in which the fill particles are encapsulated within tough water-insoluble, urea-formaldehyde polymer shells. The resulting microcapsule slurry may then be neutralized, the capsules may be separated by simply filtration, dried and used in dry, free-flowing form.
- 35 In accordance with this invention, improved capsules are provided which increase the stability of adhesive formulations. It has now been found that a specific combination of steps within the broad framework of the process disclosed in British Patent Specification No. 989,264 should be followed in preparing capsules for use in adhesives, especially those in which the capsules are in intimate contact with amine curatives.
- 40 The preferred procedure of this invention includes the steps of (1) using  $H_2SO_4$  as the acid in step 4 above, (2) using  $Na_2SO_4$  as an additive to the precondensate, (3) substituting melamine for 6% to 10% (on an equivalent weight basis) of the urea, and (4) drying the capsules at an elevated temperature in the range of 200 to 350° F. The latter step particularly seems of importance in producing capsules in which the polymer forming capsule shells are uniformly and thoroughly polymerized.
- 55 Aminoplast polymer capsule shells useful in the practice of this invention are those which comprise predominantly reaction products of urea and formaldehyde and which are capable of polymerization from a water-soluble prepolymer state under acid conditions in aqueous media (i.e. at a pH less than 7) to form substantially water-insoluble polymers. The water-soluble prepolymers are generally made by reacting urea and formaldehyde in an equivalent weight ratio of 0.6 to 1.3 parts of formaldehyde to 1 part of urea, and preferably in a weight ratio of about 1 part of formaldehyde to 1 part of urea. This is a mole ratio of 1.2 to 2.6 parts of formaldehyde to one part of urea, and preferably a mole ratio of about 2:1. Thiourea, cyanuramide (melamine), guanidine, N - alkyl ureas, phenols, sulphonamides, anilines and amines can be included as modifiers for the urea. When modifiers are used, they should be used to replace no more than 25% of the urea and preferably to replace no more than 10% of the urea, the percentage being calculated on an equivalent weight basis. For making adhesive formulations, it has been found that superior results are obtainable if 6 to 10% of melamine is added as a modifier.
- Suitable water soluble urea-aldehyde prepolymers for use in the practice of this invention are commercially available for use as adhesives, as for example, the "URAC" 110, 180 and 186 resins; the latter two are marketed by American Cyanamid as 66% and 60% solids, respectively, in aqueous solution. "URAC" 110 resin is available as a water dissolvable solid.
- Superior capsules are made from urea-formaldehyde prepolymers or precondensates prepared by the alkaline catalyzed reaction of urea and formaldehyde in water under carefully controlled conditions. Preferred conditions for the preparation of these prepolymers are pH values in the range of from 1.5 to 11.0, temperature of from 50 to 90° C, and reaction times of from fifteen minutes to 3 hours or longer in aqueous media, the higher the temperature, the less the time. Since formaldehyde is commonly available as formalin, which is a 37% solution of formaldehyde in water, usually stabilized with a small amount of methanol, it is convenient to simply add urea of formalin in the preparation of the water-soluble precondensate. The precondensate can be made at room temperature but the time required for proper precondensate formation is erratic, e.g. from 4 to 24 hours until a predominantly dimethylol urea product results.
- When the concentration of the precondensate at the time of acid addition is more than about 30 weight percent reactive solids, excessive viscosity may result, and, if less than 3 weight percent solids, the resulting capsules may be too weak and the economics of the encapsulation process decline. A preferable range of precondensate concentration in the aqueous medium, for producing superior capsules, is from 10 to 25 weight percent solids.
- In general, the microcapsule fill can be liquid, solid or gaseous, so long as it is relatively insoluble (less than 5 or 10%) in the system and inert toward reaction with other ingredients in the system; particularly the fill

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- material should be inert to attack by the polymerization catalyst acid. It is, however, in the area of liquid droplets filled capsules that the invention appears to have its greatest use.
- 5 Liquid resins are preferred for the adhesives of this invention. Epoxy resins are preferred because of their excellent adhesive and cohesive properties. However, other resins such as polyurethanes, polyesters, and polysulphide
- 10 resins can also be used depending on the end use of the adhesive.
- For reasons not readily explainable, the addition of sodium sulphate, sodium chloride, or other water soluble salt of a strong acid and
- 15 a strong base inert to the urea-formaldehyde (UF) reaction system, to the precondensate solution results in tougher capsules capable of carrying higher fill content and facilitates capsule formation in the higher pH ranges, e.g.
- 20 4 to 5. For adhesive carrying capsules, a water soluble salt addition of from 0.5 to 10%, preferably from 0.5 to 6% is desirable.  $\text{Na}_2\text{SO}_4$  is the preferred salt for encapsulating resins used in the adhesives of this invention.
- 25 During encapsulation the fill material must be maintained in the form of dispersed particles, usually as oily liquid droplets dispersed in the aqueous phase by vigorous agitation. In general, the more vigorous the agitation, the
- 30 smaller the capsules produced. However, in the practice of the invention there are other important factors which bear on capsule size control, such as the manner of precondensate preparation, acid addition rate and concentration, reaction temperature, and the type of fill
- 35 used. Epoxy resins and polysulphide resins are examples of useful fills. Particles of a solid resin or a filler may be dissolved or dispersed in the fill liquid droplets.
- 40 Preferably, the amount, in parts by weight, of fill material based on the reactive precondensate solids (not including the salt) is 0.7 to 3 parts of fill per 1 part of the precondensate solids, this range providing capsules containing from 50 to 80% fill and possessing
- 45 sufficient toughness for normal handling in operations such as paper making. For larger microcapsules or higher density fills or where more ready capsule rupture is desired, the ratio may be as high as or higher than 10:1, fill to capsule solids, providing capsules with as much as 95% fill. Where a tough relatively unbreakable bead-like capsule is desired and the amount of fill per capsule is not important,
- 50 less than one-tenth part fill to each part condensate solids can be used to provide capsules.
- After the fill material has been dispersed in the precondensate and the agitation rate properly adjusted, condensation polymerization of the urea-aldehyde precondensate may be initiated by the addition of acid to the system. In
- 60 general, any water-soluble acid can be used, so long as it will maintain the pH in the range of 1 to 5. Examples of suitable acid catalysts include formic acid, citric acid, *para* toluene
- 65 sulphonic acid, hydrochloric acid, sulphuric acid and phosphoric acid.
- When capsule shell formation is begun by acid catalyst addition to the agitated dispersion of fill in precondensate solution, it is observed that the condensation polymerization initially proceeds slowly. In fact, fill can be added after, instead of before, acid addition (but prior to shell formation). The formation of shell walls is perceived within the first hour after the pH is in the range of 1 to 5. A preferred pH range is from 1.5 to 3.0 to produce tougher more impermeable capsules. Also, in this range temperature control is easily maintained and capsule reproducibility is excellent.
- When capsules of small sizes, e.g. 25 microns and smaller, are desired, the acid should be added to the system slowly over a period of several minutes. When the reaction mixture is subjected to extended high speed agitation, smaller capsules result. If larger capsules are desired, the acid addition need not be so carefully controlled, and it may even be desirable to add the acid all at once.
- After a polymerization period of about one-half hour to one hour following acid addition, the temperature may be raised in the range of 60 to 90° C (below the boiling point of either the fill or the precondensate solution) to complete the shell formation. Preferably the reaction should be run for at least 1 to 3 hours, and more preferably for at least 2 hours, after acid addition at the desired pH range before separating the capsules or neutralizing the resultant slurry and preventing further significant polymerization. While the polymerization may be permitted to run as long as six hours or more, longer times may be required if the fill is of a nature which prohibits too much temperature rise.
- Addition of the fill material may be made directly to the precondensate solution; however since this precondensate solution is usually mildly alkaline, it is preferred to adjust the initial pH of the precondensate solution to a neutral or weakly acid state before addition of the fill material.
- In forming the adhesives of this invention, tough thoroughly polymerized shell walls are desired. In order to ensure attainment of this objective in so far as practical, the capsules are dried at an elevated temperature. Satisfactory results are obtainable by drying over a broad temperature range of 60 to 350° F, but it has been found that the toughest capsules for adhesives can be produced by drying or heat treating at temperatures of 200 to 350° F for at least the time necessary to bring the water content to 0.25% as analysed by the Karl Fischer procedure. It will be understood that the capsules should not be heated for a time sufficient to significantly degrade the fill resin.
- The invention will be further illustrated by

means of the accompanying examples in which all parts are given by weight unless otherwise indicated.

#### EXAMPLE I

5 A urea-formaldehyde resin pre-polymer solution was prepared by reacting an agitated mixture of 17.6 kg 37% Formalin, 85.2 g triethanolamine, 6.56 kg urea for two hours at 70 ° C. After this reaction period the resulting solution was diluted with 80.8 kg of cold water.

The encapsulation of ERL 2795 epoxy resin, a bisphenol - epichlorohydrin reaction product, was carried out in a 50 gallon reactor having the dimensions of 34" high  $\times$  22½" diameter with 4 baffles 2" wide fitted with a 4" flat blade turbine agitator 8" from the tank bottom as follows: The pre-polymer solution above was adjusted to a pH of 7.0 with 160 ml 3N hydrochloric acid at 22.2° C after which was added 27.2 kg of ERL-2795. The agitation speed was adjusted to 1230 rpm and agitation continued for 34 minutes to ensure equilibrium mixing prior to initiating the encapsulation reaction. The acid catalyzed polymerization reaction leading to formation of deposited shell walls of urea-formaldehyde resin was catalyzed by adding 448 ml 3N hydrochloric acid at a rate of 40 ml per minute to a pH value of 2.2. The reaction was maintained at 23.3° C for one hour after the pH was reduced to 2.2 at which time the temperature was increased to 40° C. The encapsulated epoxy resin product was recovered after overnight reaction by neutralizing (pH=7) with 27.5% sodium hydroxide, filtration and water washing of the slurry and drying in a forced air oven at 120° F. The capsule size range was 25—75 $\mu$ .

8.0 g of polyvinyl butyral resin were dissolved in 92 g of toluene which had been heated to 140 to 150° F. 32 g of 1,3 - bis-4 - piperidyl propane, an amine having 105 atomic weight units per amine group, was added to this hot solution, and the resulting mixture was agitated for two hours until the amine had completely dissolved. The mixture was then cooled to room temperature (75° F) and 80 g of the capsules (containing about 60 g of epoxy resin) were then added, and the resulting mixture agitated until the capsules were well distributed through the solution. After standing for approximately 48 hours, the capsules had settled to the bottom of the container, but could be redistributed by agitating the container.

The adhesive was tested by dipping a ½" diameter, 13 threads to the inch, 1" long, hex head can screw, into the adhesive, threads first, lifting the bolt out, and allowing the adhesive to dry on the threads. The amount of dry adhesive was usually from 0.3 to 0.45 g. After 24 hours at room temperature, and 2 hours at 160° F, the toluene solvent had evaporated,

leaving a non-tacky film of the adhesive on the threads of the bolts. The adhesive was tested by mating an appropriate sized nut to the bolt and running the bolt into the nut with 416 kg-cm of run in torque. After 24 hours, the break-loose torque was measured, with a torque wrench, and if prevailing torque was measured, the same measurement was made by recording the amount of torque required to move the bolt out of the nut after ½ to 1 full revolution from break-loose. Typical values were 692 and 664 kg-cm for break-loose torque and 388 and 444 kg-cm for prevailing torque. Values for nuts and bolts without adhesive were 291 kg-cm for break-loose torque and 0 for prevailing torque. Break-loose torque on bolts stored for 52 weeks produced a similar increase in break-loose torque.

Tests were also conducted with ⅜  $\times$  1¼ inch Grade 5 cap screws with matching nuts. All metal parts were degreased with acetone and dried before adhesive application. The bolts were dipped into the adhesive so that sufficient threads were covered to engage the nut with two threads exposed on the backside of the nut.

On these ⅜ inch screws, the adhesive covered about 0.85 inch of the threads. Excess adhesive was permitted to drain from the screws for about 10 seconds, then any additional excess material was scraped onto the edge of the can containing the liquid adhesive. Solvent removal was effected by letting the screws stand upright on the head for 24 hours at room temperature, then for 2 hours at 160° F in an oven. After this treatment, about 0.18 to 0.20 gram of adhesive containing approximately 1% solvent was left on the threads of the screw. This constituted sufficient excess so that adhesive was extruded from the mating surfaces when the screw was tested.

Ability of the adhesive to provide bonds after reuse was tested on these bolts using a procedure simulating actual use. A hardened steel washer was placed between the head of the bolt and a mild steel plate which had a hole drilled for insertion of the bolt. A second hardened steel washer was placed under the nut on the exposed side of the bolt and the nut was tightened to 31 ft. lb seating torque with at least two threads exposed outside of the nut. A 24 hour cure time at room temperature was used before the break-loose torques were measured. The bolts were resealed immediately after making the complete measurement for each cycle. Results are shown in Table I. The break-loose torque of this assembly without adhesive was 25 ft. lb. Each of the figures given is the average of 8 test samples. Similar assemblies were also tested by exposure to gasoline, oil, and water immersion, outdoor exposure, and salt spray, for one month. The adhesive in each case withstood the exposure without significant loss of adhesive properties.



TABLE I

Reuse	(PIT) Pre- vailing in Torque (kg—cm)	(ST) Seat- ing Torque (kg—cm)	(BLT) Break- loose Torque (kg—cm)	(POT) Pre- vailing Out Torque (kg—cm)
Initial	7	429	553	124
1st	90	429	443	83
2nd	37	429	373	41
3rd	21	429	346	28
4th	14	429	318	6

(<sup>1</sup>) Prevailing in torque increases as the nut is screwed on until all of the threads are engaged. This value is then a maximum until the screw is seated and is the reported value.

(<sup>2</sup>) Seating torque commercially recommended for Grade 5, 3/8 inch screws to give a fastener tension between 60 and 70% of the ultimate yield strength of the fastener material.

(<sup>3</sup>) Prevailing out torque was an average value taken at the end of the first revolution out during steady, even removal of the bolt.

5 It has also been found that the stability of  
the adhesive for long term storage can be im-  
proved by drying the capsules at elevated tem-  
peratures of 200 to 350° F. It has also been  
found preferable to use H<sub>2</sub>SO<sub>4</sub> in place of  
HCl and Na<sub>2</sub>SO<sub>4</sub> in place of NaCl in the cap-  
10 sule making procedure. Melamine can also be  
substituted for about 8% (on an equivalent  
weight basis) of the urea in order to bring  
about a further improvement in the capsule  
stability. These improved capsules, which are  
15 further described in Example VIII, enable  
the use of a wider variety of curatives than  
possible with capsules previously known. The  
capsules can also be treated with a solution of  
an alcohol such as furfuryl alcohol immediately  
before drying. This latter treatment apparent-  
20 ly has the effect of chemically "tying up" any  
amine-reactive chemical groups in the cap-  
sule shell walls, and makes the capsules more  
readily dispersible in organic solvents and  
binders.

#### EXAMPLE II

25 A mixture of 15.0 g of Versamid B—710,  
a polyamide resin made from a long chain  
aliphatic dibasic acid and a polyamide having  
a softening temperature of about 150 °F and  
an amine number of less than 100, with 20.0 g  
30 of 1,3 - bis - 4 - piperidyl propane, was heated  
to 200° F, at which temperature the mixture  
was a viscous solution. 40 g of the capsules of  
Example I were stirred into the mixture to  
give a viscous paste, with a viscosity at 200°

F of about 120,000 centipoise. This paste did  
not change in viscosity at this temperature for  
48 hours. This hot paste was applied to the  
threads of a clean, dry bolt, along one side of  
the threads as a stripe, approximately ¼ inch  
40 wide. The Versamid B—710 served as a bind-  
er for the reactive ingredients. A nut was  
threaded onto this bolt, and torqued in with  
416 kg-cm of applied pressure and allowed to  
stand 24 hours before measuring the break-  
45 loose torque. Break-loose torques of 720 kg-cm,  
748 kg-cm, 720 kg-cm, and 790 kg-cm were  
measured for four bolts coated and treated  
in the described fashion. The paste when  
cooled to room temperature hardened into a  
50 somewhat waxy solid which could be applied  
to fasteners by rubbing on at room tempera-  
ture or remelted and applied.

#### EXAMPLE III

A solution "A" was made by dissolving 25  
parts by weight of a butadiene-styrene block  
stereospecific copolymer in 75 parts by weight  
55 toluene. A second solution "B" was made by  
dissolving 50 parts by weight of Staybelite  
Ester No. 10, a hydrogenated wood resin, in  
50 parts by weight toluene. A third solution  
60 "C" was made by dissolving 5 parts by weight  
Hycar (Registered Trade Mark) 1072 (a buta-  
diene-acrylonitrile copolymer containing some  
free carboxyl groups) in 95 parts by weight  
toluene. Solution "A" (15 parts) was blended  
65 with "B" (2.5 parts) and "C" (50 parts).

After the mixture was thoroughly blended, 5.13 parts of 1,3 - bis - 4 - piperidyl propane was dissolved in the mixture and 11.25 parts of capsules (70% fill, 10 to 120 $\mu$  diameter) were stirred in until the resulting material was a homogeneous dispersion. The dispersion was coated out on a silicone release paper with a blade of approximately 20 mil thickness, to give a viscous coating on the surface of the release coating paper. After evaporation of the solvent, a film was obtained which could be stripped readily from the release paper. This film had an elongation of over 100% and the strength of the film was low. When wrapped on the threads of a  $\frac{1}{2}$ " bolt, and a nut applied, and torqued down to 416 kg-cm, after 24 hours, an average of 762 kg-cm was required to break the nut away from the bolt. Washers could also be cut from the film and used as locking means.

#### EXAMPLE IV

A mixture of 16.0 grams of imidazole, 40 grams of the capsules as used in Example I, and 50 grams of 8% polyvinyl butyral in toluene was prepared. This mixture was thoroughly blended and then applied to the threads of one-half inch 13, 1" long hexagonal head cap screws. After a 24 hour drying period at room temperature the solvent content was reduced to 30%. The bolts were then fitted with nuts which were tightened to 416 kg-cm of applied torque. After 2 $\frac{1}{2}$  days cure at room temperature, the break-loose torque was measured and found to be 707 kg-cm, 762 kg-cm,

804 kg-cm, and 804 kg-cm. The average prevailing torque to maintain the removal of the nut was 208 to 267 kg-cm.

#### EXAMPLE V

An adhesive formulation was prepared by mixing 16.0 grams of methylene-dianiline, 40.0 grams of the capsules as used in Example I, and 50.0 grams of 8% polyvinyl butyral in toluene. This mixture (after being thoroughly blended) was also applied to the threads of  $\frac{1}{2}$  inch cap screws as in Example IV. The break-loose torque was measured at the end of a 2 $\frac{1}{2}$  day room temperature cure. The break-loose torques were measured and found to be 749 kg-cm, 831 kg-cm, 721 kg-cm, and 804 kg-cm. Average prevailing torque was 416 kg-cm on this first removal of the nut.

#### EXAMPLE VI

Example I was repeated, substituting different binders for the polyvinyl butyral resin. The proportions of ingredients used are listed in Table II as are the values obtained by applying the adhesive under the head of a  $\frac{1}{2}$ " bolt of the type as described in Example I, putting the adhesive in place, and allowing the adhesive to cure.

Some of the bolts with the adhesive thereon were aged at 120° F. These bolts were then turned into place and allowed to cure. The torque required to remove the latter bolts are also recorded in Table II. The numbers given in parentheses indicate the time in weeks in which the bolts were aged at 120° F.

TABLE II

Sample No.	Binder	Parts Binder	Capsules, Parts	1,3-bis-4-piperidyl propane	Break-Loose Torque	
					Initial	Aged Adhesive (aged 3 wks.)
A	25% butadiene styrene block copolymer in toluene	10.6	64.0	24.4	485	374
B	25% low molecular weight butadiene styrene block copolymer in toluene	10.6	65.0	24.6	374	374

#### EXAMPLE VII

Adhesive formulations were prepared using the capsules as used in Example I with a liquid polyamid resin (Versamid 125) as the curing agent. The liquid polyamid capsule mixture was made solid and non-tacky by the addition thereto of appropriate polymeric

binders. The amounts of capsules, binder, and curing agent are listed in Table III. The values for break-loose torque obtained by applying the adhesive formulation to the underside of the heads of  $\frac{1}{2}$ " bolts of the type described in Example I, tightening the bolts in place, and allowing the adhesive to cure, are

also given in Table III. Some of the bolts with the adhesive thereon were aged at 120° F before being tightened into place. The values

obtained for back-off torque after this amount of aging are also given in Table III.

5

TABLE III

Sample No.	Binder	Parts Binder	Capsules, Parts	Curing Agent Parts	Break-Loose Torque (kg—cm)	
					Initial	Aged, 3—5 wks.
A	25% butadiene-styrene block copolymer in toluene	17.0	47.4	34.5	514	444
B	25% low molecular weight butadiene-styrene block copolymer in toluene	10.0	52.5	37.5	444	348
C	10% GR—S type butadiene-styrene copolymer in toluene	4.0	56.0	40.0	528	361
D	10% polyvinyl butyral in toluene	7.6	54.0	38.4	500	444
E	20% isobutylene rubber (GR—I) in toluene	5.9	54.9	38.2	528	416

## EXAMPLE VIII

10 A urea-formaldehyde resin prepolymer solution was prepared by reacting an agitated mixture of 248 kilograms of 37 percent formalin solution, 1.52 kilograms of triethanol amine, 85.3 kilograms of urea and 15.6 kilograms of melamine for two hours at 70° C. After this reaction period the resulting solution was diluted with 527 kilograms of cold deionised water. Then 8.77 kilograms of sodium sulphate was added. The reaction was carried out in a nominal 100-gallon capacity stainless steel vessel equipped with cover, agitator, and heating and cooling means. Dilution was carried out in the encapsulation reactor. The encapsulation of ERL—2795 epoxy resin, a bis phenol A epichlorohydrin reaction product, was carried out in a nominal 25 350-gallon capacity, fully baffled, stainless steel tank. The tank specifications were 60 inches high, 41½ inches in diameter with a dished bottom and a baffle width of 3½ inches. Agitation was by means of a 7 inch diameter, 30 6-blade, flat-blade turbine located 19 inches from the bottom of the tank. The prepolymer solution described above was adjusted to a

pH of 7, with about 1000 milliliters of 6 normal sulphuric acid at 26° C, after which were added 360 kilograms of ERL—2795. The agitation speed was adjusted to 650 rpm; and agitation continued for 30 minutes to ensure equilibrium mixing prior to and initiating the encapsulation reaction. The shell-forming polymerization reaction was catalysed by adding 22 liters of 6 normal sulphuric acid at a rate of 700 milliliters per minute to a pH value of 2.1. The reaction was maintained at 26° C for one hour after the pH was reduced to 2.1, at which time the temperature was increased to 55° C. After four hours at this temperature, 26 kilograms of furfuryl alcohol were added and the reaction continued for 30 minutes at that temperature. The alcohol treatment apparently has the effect of chemically "tying up" any reactive chemical groups in the capsule shell walls. The alcohol treated capsules are much more readily dispersible in organic solvents and binders. The encapsulated epoxy resin product was recovered after one hour by neutralising to a pH of 7 with 27.5 percent sodium hydroxide, filtration and water washing of the slurry and drying in a forced

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air oven at 107° C. The capsule size range was 25 to 100 microns.

5 8.0 g of polyvinyl butyral resin were dissolved in 92 g of toluene which had been heated to 140 to 150° F. 32 g of 1,3 - bis-  
 10 4 - piperidyl propane were added to this hot solution and the resulting mixture was agitated for two hours until the amine had completely dissolved. The mixture was then cooled to  
 15 room temperature (75° F) and 80 g of the capsules (containing about 60 g of epoxy resin) were then added, and the resulting mixture agitated until the capsules were well distributed through the solution. After standing for approximately 48 hours, the capsules were  
 20 packed in the bottom of the container; however, they could be redistributed by placing the container on a roll mill, and rolling the formulation for approximately 30 minutes at a relatively low speed, for example, 60 RPM.

The adhesive was tested by dipping a  $\frac{1}{2}$  inch diameter, 13 threads to the inch, one inch long, hexhead grade 2 capscrew into the adhesive, threads first, lifting the screw out and  
 25 holding the screw at a 45° angle for approximately 10 seconds while the adhesive drained into the liquid. Excess adhesive was then scraped from the bottom of this screw, and the screw was allowed to stand at room temperature for 24 hours on the head with the threads  
 30 upward to remove most of the toluene solvent. The screw was then placed in a 160° F oven for four hours to remove the last traces of solvent in order to allow maximum performance of the adhesive. The amount of dry adhesive on this screw was usually from 0.3 to 0.45 gram.

The adhesive was tested by mating an appropriate sized nut to the bolt and running the bolt into the nut with 416 kg-cm of run in torque. After 24 hours, the break-loose torque was measured, with a torque wrench, and if prevailing torque was measured, the same measurement was made by recording the  
 45 amount of torque required to move the bolt out of the nut after  $\frac{1}{2}$  and 1 full revolution from break-loose. Typical values were 692 and 664 kg-cm for break-loose torque and 388 and 444 kg-cm for prevailing torque. Values for nuts and bolts without adhesive were 291 kg-cm for break-loose torque and 0 for pre-

vailing torque. Break-loose torque on belts stored for 52 weeks produced a similar increase in break-loose torque.

#### EXAMPLE IX

The improved stability of adhesives made with resins contained in capsules prepared in accordance with this invention compared with those previously available was demonstrated by preparing several adhesive formulations in which several different curatives were used. In all cases the stoichiometric amount of curative used was based upon the equivalent weight of the curative compared with the equivalent weight of the resin in the capsules. Both batches of capsules were made such that they contained 70% fill and had average diameters of about 40 to 50 microns. The difference in the two capsules was that one batch was made by the procedure described in Example I (using HCl as the condensation catalyst and omitting the melamine modification and the heat treatment) while the second batch of capsules was prepared by the procedure described in Example VIII above. The viscosity of each composition at room temperature was measured with a Brookfield viscometer. The mixture was then aged at 160° F for the period of time indicated in Table I and a subsequent measurement of the viscosity was made. Direct comparison was made with dimethylamino-propylamine L 0814 (a commercially available epoxy curative), 1,3 - bis - (4 - piperidyl) - propane. An additional comparison was made using diethylenetriamine and triethylenetetraamine with the capsules. The diethylenetriamine was used in the formulation with the capsules of Example I, and the triethylenetetraamine was used with the capsules of Example VIII, these two amines being sufficiently similar to make the comparison meaningful. Using the 1,3 - bis - (4 - piperidyl) - propane, the adhesive had sufficient stability with the capsules of Example I to be commercially useful. However, even here significant improvement was effected by the use of the capsules prepared in the procedure described above. Results of the comparisons which illustrate the great improvement in adhesive stability achieved by this invention are given in Table IV.

TABLE IV

Amine	Capsules	Viscosity, centipoise		Aging time, days
		Original	After 160° F Aging	
Dimethyl amino propyl amine	Ex. VIII	50	100	9
	Ex. I	50	gel	1
Hydroxyethyl diethylene triamine	Ex. VIII	26,000	32,000	9
	Ex. I	26,000	gel	7
Triethylene tetramine	Ex. VIII	250	600	9
Diethylene triamine	Ex. I	250	gel	2
1,3-bis-(4-piperidyl)-propane	Ex. VIII	300	300	9
	Ex. I	300	1050	6

## WHAT WE CLAIM IS:—

1. A mechanical fastener having on abutment surfaces thereof a coating of a locking cement which is pressure-activatable and self-curing at ambient temperatures to give a firmly adherent bond and which comprises microscopically small capsules containing therewithin a liquid resin, the capsules being rupturable upon application of pressure, a substantially non-volatile curing agent for the resin which is miscible therewith, and a non-hygroscopic substantially non-tacky and water-free organic polymeric binder in which the microcapsules and curing agent are homogeneously dispersed.

2. A mechanical fastener as claimed in Claim 1 in which the abutment surfaces comprise a threaded portion of the fastener.

3. A fastener as claimed in Claim 1 or Claim 2 in which the capsules have infusible aminoplast polymer shells.

4. A fastener as claimed in Claim 3 in which the shells comprise a melamine modified urea-formaldehyde condensation polymer, the amount of melamine being sufficient to constitute a 6 to 10% substitution on an equivalent weight basis for the urea.

5. A fastener as claimed in any preceding claim in which the liquid resin is a liquid polyepoxide resin.

6. A fastener as claimed in any preceding claim in which the curing agent is a room temperature solid low volatility amine curing agent which is capable of storage at 120° F

with exposure to the atmosphere for at least one week without loss of more than 2% thereof due to vapourisation, the amine having at

least about 50 atomic weight units per amine group.

7. A fastener as claimed in Claim 6 in which the amine curing agent is 1,3 - di - 4 - piperidylpropane.

8. A fastener as claimed in Claim 6 in which the amine is imidazole.

9. A fastener as claimed in any preceding claim in which the binder is polyvinyl butyral.

10. A fastener as claimed in any preceding claim in which the capsules have been dried at a temperature of 200 to 350° C to a water content of less than 0.25%.

11. A mechanical fastener substantially as herein described with reference to the accompanying drawing.

12. A mechanical fastener substantially as herein described in any of the Examples.

13. A staple latent room temperature curable adhesive cement composition which can be applied on surfaces to be bonded to form a stable solid substantially non-tacky coating which is pressure-activatable and self-curing at ambient temperatures to give a firmly adherent bond, comprising microscopically small capsules containing therewithin a liquid polyepoxide resin, the capsules being rupturable upon application of pressure, a substantially non-volatile curing agent for the polyepoxide resin which is miscible therewith, and a non-hygroscopic substantially non-tacky and water-free organic polymeric binder in which the microcapsules and curing agent are homogeneously dispersed.

14. A composition as claimed in Claim 13 useful as a fastener sealant in which the curing agent is an amine which will convert the

polyepoxide resin at room temperature to a hard infusible state within eighteen hours after rupture of the capsules.

5 15. A composition as claimed in Claim 13 or Claim 14 in which the binder is a room temperature solid thermoplastic resin which can be applied to a fastener in a molten condition at elevated temperatures.

10 16. A composition as claimed in Claim 15 in which the binder is polyvinyl butyral.

17. A composition as claimed in Claim 13 or Claim 14 in which the binder is a rubbery polymeric material, the composition being in the form of a thin film.

15 18. A composition as claimed in any of claims 13 to 17 in which the binder, capsules and curing agent are contained in a volatile non-polar organic solvent compatible with the capsules.

20 19. A composition as claimed in Claim 18 in which the solvent is toluene.

20. A composition as claimed in any of claims 13 to 19 in which the capsules have pressure rupturable aminoplast polymer shells.

25 21. A composition as claimed in Claim 20 in which the shells comprise a melamine modified urea-formaldehyde condensation polymer, the amount of melamine being sufficient to constitute a 6 to 10% substitution on an equivalent weight basis for the urea.

30 22. A composition as claimed in any of claims 13 to 21 in which the curing agent is a room temperature solid low volatility amine curing agent for the polyepoxide resin, the amine curing agent being capable of storage at 120° F with exposure to the atmosphere for at least one week without loss of more than 2% thereof due to vapourisation, the amine having at least about 50 atomic weight units per amine group.

40 23. A composition as claimed in Claim 22 in which the amine is 1,3 - di - 4 - piperidylpropane.

45 24. A composition as claimed in Claim 22 in which the amine is imidazole.

25. A composition as claimed in any of claims 13 to 24 in which the capsules have been dried at a temperature of 200 to 350° F to a water content of less than 0.25%.

50 26. A stable latent room temperature curable adhesive cement composition substantially as herein described in any Example.

55 27. A process of preparing a stable latent pressure activatable adhesive cement composition based on micro-encapsulated water in-

soluble liquid polyepoxide resin droplets with-  
in water-insoluble urea-formaldehyde shells  
and a curing agent for the resin without the  
shells, said shells being impermeable to the  
resin and the curing agent, which comprises (1) 60  
providing an aqueous solution of a water-sol-  
uble, low molecular weight precondensate of  
urea and formaldehyde comprising predomi-  
nantly dimethylol urea containing 6 to 10% 65  
melamine by weight of the urea, the solids con-  
tent of the precondensate being in the range  
of 3 to 30% and the mole ratio of formalde-  
hyde to total urea and melamine being in the  
range of 1.2:1 and 2.6:1, the precondensate  
containing 0.5 to 10%  $\text{Na}_2\text{SO}_4$ , (2) adding the 70  
liquid polyepoxide resin fill to the aqueous  
precondensate solution, the fill material being  
substantially water-insoluble and inert toward  
reaction with the precondensate and its sub-  
sequent polymerization products under the 75  
polymerization conditions, then, (3) while  
maintaining the resulting system substantially  
free of wetting agents, subjecting the system  
to vigorous agitation to disperse the fill mater-  
ial as resin droplets in the precondensate solu- 80  
tion, (4) while continuing vigorous agitation  
to maintain the dispersion of resin droplets in  
the precondensate, gradually adding sulphuric  
acid to the dispersion in just sufficient amount  
to bring the dispersion within a pH range of 85  
1.5 to 3.0 and thereby causing polymeriza-  
tion of the precondensate, (5) continuing poly-  
merization of the precondensate to a water-  
insoluble polymer for at least two hours while  
continuing vigorous agitation of the dispersion, 90  
whereupon the polymer condenses as tough,  
water-insoluble, continuous shells around the  
liquid polyepoxide resin droplets and provides  
an aqueous slurry of microcapsules, drying  
the capsules at a temperature of 200 to 350° 95  
F, and mixing the resultant capsules together  
with the curing agent for the liquid poly-  
epoxide resin and a polymeric binder.

28. A process for preparing a latent room  
temperature curable adhesive cement compo- 100  
sition substantially as herein described in any  
Example.

29. A latent room temperature curable ad-  
hesive cement composition when prepared by a  
process as claimed in Claim 27 or Claim 28. 105

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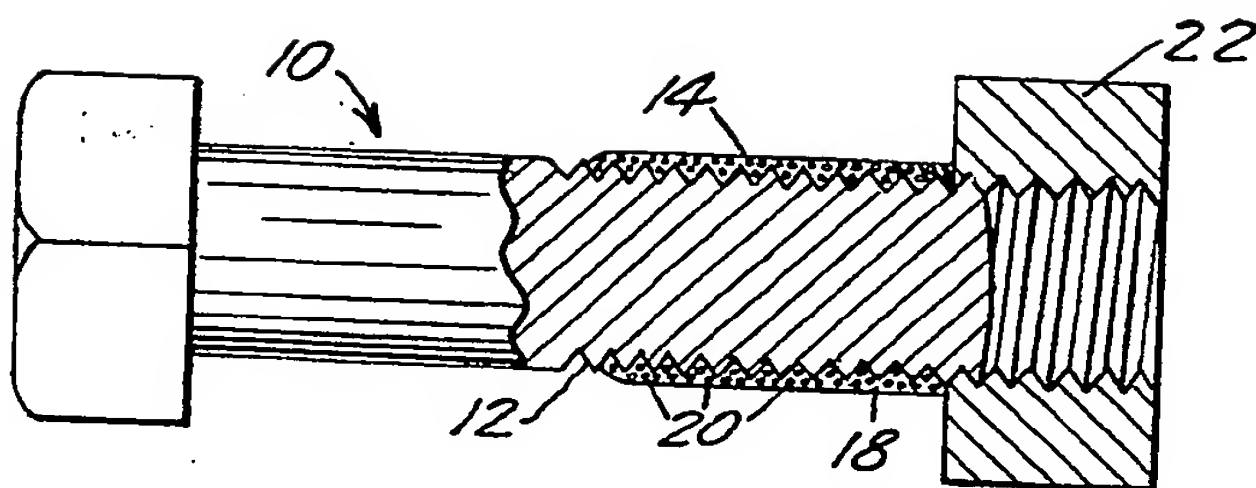


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COMPLETE SPECIFICATION

1 SHEET

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